

A New High Resolution Technique for the Study of Metal-Containing Radicals

Molecular free radicals containing a transition metal bonded to a first row atom have traditionally been difficult to study. They generally require high temperatures to be formed in the gas phase for high resolution studies and possess a multitude of low-lying excited electronic states due to incompletely filled molecular orbitals derived from the metal d-orbitals. For these reasons, much of our knowledge of metal-carbon, metal-oxygen and metal-nitrogen bonding comes from emission-based studies of the diatomics at high temperatures. More complex species containing a molecular ligand, are generally too reactive or insufficiently stable to maintain sufficient concentrations at high temperatures and in any case generally have lower emission quantum yields. However, the study of these species is important because they are models for the bonding interactions which occur at the active sites in heterogeneous catalytic processes. In the petrochemical industry, for example, such processes are of extreme economic importance. The active sites are generally assumed to involve surface defects, corners or steps where a metal atom is coordinatively unsaturated or in some other way activated. Even basic questions regarding the coordination number, charge distribution and stereochemistry remain unanswered in many cases.

A more fundamental understanding of the steps involved in heterogeneous chemistry occurring on metal or supported metal catalysts must necessarily involve a molecular description of the intermediate species. In this way, progress towards the rational design of future catalysts may be made. Spectroscopic studies of representative smaller molecules can provide the information that enables the testing and refinement of potential energy surfaces and force field calculations for actual catalysts. Quantities such as fine and hyperfine parameters and dipole moments from high resolution spectroscopy give direct information on bonding, electronic structure and charge distributions for comparison with results of model-based calculations.

We have developed experimental techniques that permit the study of cold, isolated samples of this type of species by direct absorption of a high resolution laser. Previous measurements on these molecules had relied upon fluorescence-based techniques. This is a severe limitation since species larger than diatomics or simple triatomics generally show decreasing fluorescence quantum yields as internal conversion, dissociation and other competitive decay mechanisms open up. Figure 1 shows a schematic diagram of the basic experiment. Metal-containing radicals were generated by the reaction

of laser ablated metal atoms with a reactant seeded in a supersonic expansion of an inert gas. Reactive intermediates are quenched and cooled as the expansion proceeds, then probed under collision-free conditions by

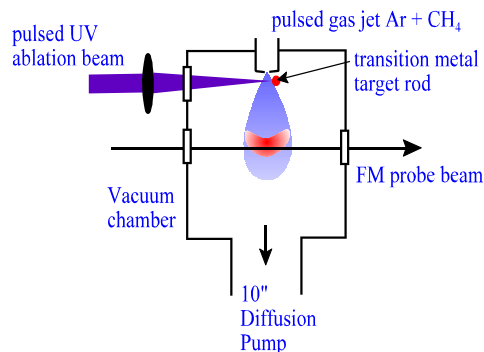


Figure 1: Schematic diagram of the experiment. Different reactive gases, diluted in argon, are introduced to form different molecular radicals.

the beam from a frequency-modulated, single-frequency c.w. laser. The laser power absorbed was measured at quantum-noise limited sensitivity using the techniques we have previously developed for the study of molecular transients in combustion chemistry.

Initial results for several diatomics have been obtained. These are proof-of-principle experiments which allow us to compare with the results of laser induced fluorescence experiments previously reported by other workers. Two titanium-containing species are described

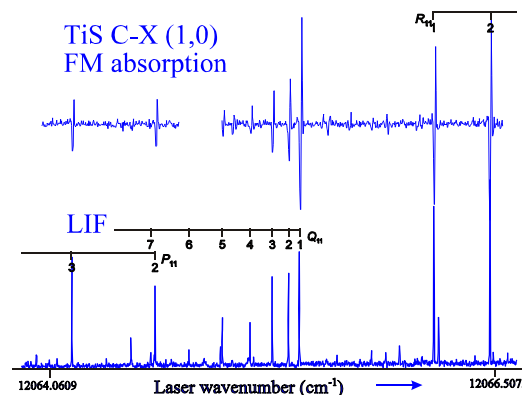


Figure 2: Part of the C-X spectrum of TiS comparing FM transient absorption to laser induced fluorescence (from Prof. T. Steimle, Arizona State University). There is a gap in the FM spectrum due to a section that was not recorded.

here. First, titanium sulfide was produced by the reaction of Ti atoms with CS₂ in an argon expansion. Figure 2 shows part of the C ³Δ₁ - X ³Δ₁ band system of TiS near

12060 cm^{-1} and compares results from our laboratory to some state-of-the-art LIF spectra kindly provided to us by Prof. Tim Steimle (Arizona State). The latter exhibit slightly narrower line widths since the ASU experimental apparatus uses a skimmed beam source. However the BNL spectrum is rotationally colder, and shows little evidence for population in the higher spin orbit components. For example, $Q_{22}(2)$ in the LIF spectrum is just above $R_{11}(1)$. The FM spectrum was recorded by integrating just the first microsecond of the transient absorption waveform; rotationally and translationally warmer spectra can be collected at later times. Overall, the comparison is very encouraging. Given the apparent lower sample temperature, the FM absorption spectrum shows all the expected features and the sensitivity of the two techniques appear to be similar.

As a more challenging test, we have investigated the $E^3\Pi - X^3\Delta$ transition in TiO. This band system is known to have a rather small transition dipole moment, [See S. R. Langhoff, *Astrophys. J.* **481** 1007-1015 (1997)] since it is primarily a $4p\pi - 3d\delta$ transition on the Ti atom which is much weaker than the $4p-4s$ atomic transition. The latter is responsible for the known radical transitions at shorter wavelengths that are calculated to be more than $10\times$ stronger. This notwithstanding, an accurate measurement of the rotational structure of the band system is important for comparison with the spectra of M-type stars where TiO emission and absorption dominates the stellar spectrum throughout the visible and near-IR. Figure 3 shows an example of our spectra, again recorded in absorption using the transient FM technique

previously reported and will allow refinement of the molecular parameters and give improved laboratory line positions that will be important for the calibration of astronomical observations.

Future work in this area is planned on TiC, a species for which there is very little experimental information available, despite its probable importance in titanium-carbon plasma chemistry used in the production of industrial hard coatings. Of course, the major attribute of this experiment compared to more usual LIF-based techniques is the ability to study non-fluorescent species and it is this area that we intend pursue later. Of particular interest are metallo-carbohedrene (met-car) species that are made up of 3-dimensional cages of, for example titanium and carbon atoms. These are known to be formed in sources similar to ours [see, for example, Muñoz et al, *J. Phys. Chem A* **103**, 4762-4768 (1999)] but there is little or nothing known of their optical spectra.

References to published work:

- ¹ J. C. Bloch, R. W. Field, G. E. Hall and T. J. Sears, *J. Chem. Phys.* **104**, 1717-1718 (1994).
- ² T. C. Steimle, M. L. Costen, G. E. Hall and T. J. Sears, *Chem. Phys. Letts.*, **319**, 363-367 (2000).

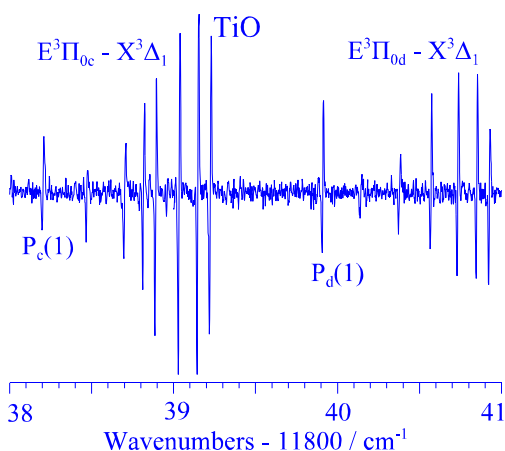


Figure 3: Central section of the TiO E-X spectrum observed by FM transient absorption in a jet-cooled Ti-metal ablation source.

and a jet cooled metal ablation source. Aside from our work, the most recent experimental work was reported in 1991, where medium resolution LIF using a pulsed dye laser was observed. The spectrum shown in figure 3 represents a considerable improvement over that